

# ES&H manual

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## Environment, Safety, and Health

### Volume II

#### Part 18: Pressure/Noise/Hazardous Atmospheres

## Document 18.4 Hydrogen

Recommended for approval by the ES&H Working Group

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New document or new requirements

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\* Editorial revision

## 18.4

### Hydrogen

#### 1.0 Introduction

This document describes the hazards associated with hydrogen gas and provides requirements for Laboratory operations involving the use or generation of hydrogen gas. These requirements apply to all hydrogen gas systems and associated equipment. They do not apply to liquid hydrogen, except where a hydrogen gas is produced from a liquid source or a system.

All uses of hydrogen at LLNL require an environmental, safety and health (ES&H) Team review to assess the possibility of forming a flammable or explosive mixture in the work area. The ES&H Team will also help determine which regulations, controls, and documentation requirements apply to a particular project involving hydrogen.

The requirements for gaseous hydrogen systems used at LLNL are based on a system's size and its potential for forming an explosive mixture in air. Explosion-potential systems contain sufficient hydrogen in vessels and piping to produce a flammable or explosive mix if released into the immediate area or enclosure (normally 4% in air). Nonexplosion-potential systems contain less hydrogen than is needed to produce such a mixture. The Occupational Safety and Health Administration (OSHA) regulations apply to hydrogen systems with a capacity of 400 standard cubic feet or more. Various National Fire Protection Association (NFPA) and Compressed Gas Association (CGA) standards cover hydrogen systems of all sizes. These standards include requirements for fire-resistant construction, special ventilation, explosion venting, spark prevention, and explosion-proof electrical systems (National Electric Code (NEC) Class I, Group B).

A list of the regulations and requirements that govern this document is provided in Section 5.0.

#### 2.0 Hazards

Hydrogen possesses several unique properties that render it more hazardous than most other flammable gases. Hydrogen has no warning properties. It is a clear, colorless, odorless, and tasteless gas. It burns with an extremely hot, but nonluminous, flame. Hence, even the flame of burning hydrogen has few warning properties, making the extent of hydrogen fires difficult to judge.

Hydrogen has an unusually large flammability range. It can form ignitable mixtures between 4 and 75 percent by volume in air. The range for explosive mixtures is also very broad. Given confinement and good mixing, hydrogen can be detonated over the range of 18 to 59 percent by volume in air. The energy content per weight of a stoichiometric mixture of hydrogen and air is about the same as that for the explosive TNT, although much less energy is converted to pressure waves during detonation.

Hydrogen also has an extremely low ignition-energy requirement. A 20- $\mu$ J spark can ignite a stoichiometric hydrogen/air mixture. (This is 10 times less than what is required to ignite a gasoline/air mixture.) Such sparks can be generated by virtually all types of electrical equipment as well as by static charges on clothing or personnel. The auto-ignition temperature for hydrogen is 585°C.

### 3.0 Controls for Working with Hydrogen

Before work can start using hydrogen, the requirements in this section must be met. Table 1 gives an overview of the requirements for hydrogen systems used at LLNL.

#### 3.1 Engineered Controls

Typically, the hazards of hydrogen can be controlled through proper engineering and careful use of the material (i.e., using the gas only in selected locations, limiting the amount of hydrogen available, practicing good pressure-system engineering, controlling ignition sources, and training personnel). Once the hazards are evaluated, select appropriate controls tailored to the hazard level. Use engineered controls rather than administrative or procedural controls whenever possible.

##### 3.1.1 Hydrogen Gas System Design

**General.** Hydrogen gas systems should be designed for ease of operation and maintenance (e.g., changing cylinders). All storage containers, piping, valves, regulating equipment, and other accessories must be readily accessible and protected against physical damage and tampering. The piping, tubing, and fittings in all hydrogen systems – as well as valves, gauges, regulators, and other accessories – shall be suitable for hydrogen service and for the pressures and temperatures involved.

Additionally, hydrogen containers shall be designed, constructed, and tested in accordance with the requirements specified in Document 18.1, “Pressure,” and related documents in the *Environment, Safety, and Health (ES&H) Manual*. Mobile hydrogen supply units shall be electrically bonded to the system before discharging hydrogen.

**Table 1. Overview of requirements for hydrogen systems.**

If the system is	Then
A gaseous hydrogen system with flammable or explosion potential (>4% concentration) <sup>a</sup>	<ul style="list-style-type: none"> <li>Follow the requirements in this document. Contact the ES&amp;H Team for additional requirements that may be necessary.</li> <li>Prepare an Engineering Safety Note (ESN) if a non-DOT/ASME vessel is used or line pressure exceeds 60 psig. Note that an ESN is not required when the system meets all Plant Engineering – Livermore (PEL) standards.</li> <li>Prepare an operational safety plan (OSP) or incorporate safety controls into the facility safety plan (FSP).</li> </ul>
A gaseous hydrogen system with no flammable or explosion potential (<4% concentration)	<ul style="list-style-type: none"> <li>Follow the requirements in this document. Contact the ES&amp;H Team to verify calculations and determine if a safety plan is required.</li> <li>Prepare an Engineering Safety Note (ESN) if a non-DOT/ASME vessel is used or line pressure exceeds 60 psig. Note that an ESN is not required when the system meets all Plant Engineering – Livermore (PEL) standards.</li> </ul>
A liquid hydrogen system	<ul style="list-style-type: none"> <li>Contact the ES&amp;H Team for requirements. This document does not apply to liquid hydrogen systems. However, it does apply to any gas produced by liquid systems. Minimum requirements for these systems can be found in OSHA 29 CFR 1910.103(c).</li> <li>Prepare an Engineering Safety Note (ESN) if a non-DOT/ASME vessel is used or line pressure exceeds 60 psig. Note that an ESN is not required when the system meets all Plant Engineering – Livermore (PEL) standards.</li> <li>Prepare an operational safety plan (OSP) or incorporate safety controls into the facility safety procedure (FSP).</li> </ul>

<sup>a</sup> This addresses the possibility of a hydrogen leak or discharge forming a sufficient hydrogen air concentration to produce a flammable or explosive mixture in an enclosed space or area, regardless of the system's total hydrogen volume.

Consider the following factors when designing hydrogen systems:

**Embrittlement.** Many metals undergo embrittlement upon exposure to hydrogen. Thus, it is important to select suitable materials to safeguard against this condition. Austenitic stainless steel, monel, copper, and aluminum are generally satisfactory for hydrogen use. Cast iron pipe and fittings are not suitable and shall not be used.

**Flammable Mixtures.** Confined hydrogen/air mixtures can detonate instead of burn. Hence, it is imperative to prevent the formation of flammable hydrogen/air mixtures in the system. Evacuate hydrogen systems or render them inert, both before and after use. Consider methods for inert gas purging of systems that are cycled frequently. Providing simple purge connections may be sufficient for systems that are not normally exposed to air.

When air or other oxidizing gases connect to a hydrogen system, install a check valve on the oxidizer supply and flash arrestors on the hydrogen supply. Refer to the manufacturer's catalog for both check valves and flash arrestors to verify that they have been designed for hydrogen use.

**Ventilation.** Hydrogen shall be used only in well-ventilated areas. The amount of ventilation required will vary in each case depending on the total supply of hydrogen, the rate of use or generation, and the venting arrangement from the process or hydrogen system. The ES&H Team can provide an evaluation in each case. As a general rule, most laboratories have sufficient ventilation to permit the use of small amounts of hydrogen without major modifications.

**Ignition Sources.** The system designer shall ensure that hydrogen is not exposed, under any condition, to unintended ignition sources such as open flames, electrical equipment, or heating devices. Enclosures shall provide adequate ventilation, and all electronic and electrical equipment should be designed and rated for hydrogen use. This may require use of NEC Class I equipment and wiring. Electrically bond and ground all noncurrent-carrying metal parts to remove static charges.

For all hydrogen gas systems, it may be necessary to

- Vent normal effluent and pressure-relief devices outdoors or into a suitable exhaust duct.
- Avoid or carefully locate spark-producing motors and make-or-break electric contacts.
- Place the system in a fume hood or ventilated enclosure.

Additionally, explosion-potential systems and special applications may require purged enclosures for potential ignition sources.

### 3.1.2 Hydrogen Supply Location and Cylinder Storage

Hydrogen supplies should be located outside buildings, and the gas should be piped to the laboratory at the lowest usable pressure. If possible, gas drops should be kept to 10 psi maximum, as specified in Plant Engineering Standard PEL-M-13200, *Laboratory Industrial Gas Drops*. The line pressure in the distribution system should not exceed 60 psi. Gas systems with greater pressure require an Engineering Safety Note and are subject to additional NFPA requirements.

Store extra hydrogen cylinders in well-ventilated outdoor locations, away from flammable and combustible materials. Hydrogen cylinders shall be stored at least 20 ft from all oxidizing gases or be separated by a noncombustible, fire-resistant barrier with

at least a half-hour rating. Permanently installed containers shall have substantial noncombustible supports on firm noncombustible foundations.

Post signs at all hydrogen storage locations that read:

“DANGER — HYDROGEN — FLAMMABLE GAS — NO SMOKING — NO OPEN FLAMES.”

Check with the ES&H Team fire protection engineer for more information on storage compliance requirements.

### 3.1.3 Hydrogen Alarms

Fixed hydrogen-detection devices and alarms are required for all systems involving large quantities of hydrogen where long-term leaks could create an explosive mixture. For instance, alarms are typically required in facilities serviced by tube trailer banks, but are not necessary in systems with fewer than four full-sized cylinders because a leak sufficient to create an explosion would probably exhaust the hydrogen supply before the Fire Department could respond.

Where monitoring devices are used, for example, a hydrogen leak will trigger the local evacuation alarm alerting the Emergency Communications Center in Building 313 of the situation. This allows the Emergency Management Division (Fire Department) to respond and shut off the hydrogen supply, preventing a potential fire or explosion.

## 3.2 Administrative Controls

### 3.2.1 Documentation

When applicable, the design of hydrogen systems shall be documented in one of the following ways:

- An Engineering Safety Note (ESN) is required for all vessels and gas cylinders, except those that are ASME- or DOT-certified and have not been modified. An ESN is required for hydrogen piping systems with pressure greater than 60 psi.
- An Operational Safety Plan (OSP) or a Facility Safety Plan (FSP) is required for any system that requires an ESN. An OSP or FSP may also be required for systems that do not require an ESN.
- A label, tag, or other record indicating that the system is in accordance with Plant Engineering–Livermore (PEL) standards. Manifolds and piping covered by PEL standards do not require an ESN.

Refer to Document 18.1 and Document 18.2, “Pressure Vessel and System Design,” in the *ES&H Manual* for details on system design documentation.

When the pressure, quantity, or use of hydrogen in any given operation is judged by the ES&H Team or the Responsible Individual as significant, the hazards and controls for each activity—including the minimum training requirements and emergency shutdown procedures—shall be documented in an OSP or FSP. A “significant operation” includes

- Any operation in an enclosed space or area capable of creating hydrogen air concentration greater than four percent.
- Hydrogen systems with line pressures greater than 60 psi.
- Hydrogen systems containing more than 3,000 ft<sup>3</sup> of hydrogen gas.
- Systems using liquid hydrogen. (Liquid hydrogen is not covered by this document.)

Additionally, prepare and use work procedures or operational checklists for all but the simplest operations. (See Document 3.4, “Preparation of Work Procedures,” in the *ES&H Manual* for details.) Safety plans typically are not necessary for small quantities of hydrogen gas or low pressures.

### 3.2.2 Training

The most important factor in preventing accidents is applying knowledge acquired through on-the-job training and formal courses. Having a general understanding of hydrogen hazards and knowing the specific issues associated with a particular hydrogen system are critical. Special training in the design and use of hydrogen systems is available (Courses HS5050-W, “High Pressure Safety,” and HS5060-W, “Pressure Seminar for Engineers”). These courses cover procedures for controlling ignition sources and preventing hydrogen embrittlement.

### 3.2.3 Procurement

Hydrogen cylinders are on the Controlled Item List for the Procurement and Materiel Department. Therefore, the Hazards Control Department **shall** review purchase requisition for hydrogen cylinders.

## 4.0 Responsibilities

General responsibilities for all workers are described in Document 2.1, “Laboratory & ES&H Policies, General Worker Responsibilities, and Integrated Safety Management,” in the *ES&H Manual*. Specific responsibilities with for work involving hydrogen are listed under each title below.

### 4.1 Responsible Individual

- Assure project safety and that workers comply with the requirements in this document.
- Provide a system designer to ensure proper engineering, materials selection, and control of ignition sources.
- Prepare the IWS, ESN, work procedures, and OSP and provide input for FSPs as required.
- Maintain each hydrogen system in a safe operating condition.

### 4.2 Support Organizations

These organizations can provide the Responsible Individual assistance with hydrogen-related issues.

#### 4.2.1 ES&H Team

- Provide support on all ES&H issues.
- Help the Responsible Individual evaluate ventilation requirements for hydrogen systems.
- Specify when hydrogen alarms are required, which alarms are to be connected to the Emergency Communications Center, and the type and location of hydrogen detection systems.
- Help establish maintenance and calibration requirements for fixed hydrogen-detection systems and alarms.
- Perform periodic visual checks to verify operational readiness.

#### 4.2.2 Plant Engineering

When requested, Plant Engineering will help maintain and calibrate all installed hydrogen alarm systems.

## 5.0 Work Standards

8 CCR 450-560, "Unified Pressure Vessel Safety Orders."

29 CFR1910.103, "Hydrogen."

29 CFR1910.110, "Storage and Handling of Liquefied Petroleum Gases."

29 CFR1910.132, "Subpart I Personal Protective Equipment."

49 CFR100-199, "Hazardous Material Transportation."

29 CFR1910, Subpart J, "General Environmental Controls."

29 CFR1910, "Subpart M, "Compressed Gas and Air Equipment."

29 CFR1910, Subpart Q, "Welding, Cutting, and Brazing."

ANSI/B31.1, "Power Piping Code."

ASME Boiler and Pressure Code, Section VIII, Divisions 1 and 2, "Pressure Vessels Division."

NFPA 45, "Laboratories Using Chemicals."

NFPA 51B, "Welding, Cutting and Allied Processes."

ACGIH *TLVs and BEIs: Threshold Limit Values for Chemical Substances and Physical Agents*, 2002 (excluding Biological Exposure Indices, TLVs for Physical Agents, and Biologically Derived Airborne Contaminants).

Compressed Gas Association, Pamphlet P-1, *Safe Handling of Compressed Gases in Containers* (1991).

Compressed Gas Association, Pamphlet P-12, *Safe Handling of Cryogenic Liquids* (1993).

Compressed Gas Association, Pamphlet S-1.1, *Pressure Relief Device Standards, Part I, "Cylinders for Compressed Gases"* (1995).

Compressed Gas Association, Pamphlet S-1.2, *Pressure Relief Device Standards, Part 2, "Portable Tanks for Compressed Gases"* (1995).

Compressed Gas Association, Pamphlet S-1.3, *Pressure Relief Device Standards, Part 3, "Compressed Gas Storage Containers"* (1995).

DOE M 440.1-1, *DOE Explosives Safety Manual*.

NFPA 50A, "Gaseous Hydrogen Systems at Consumer Sites."

NFPA 50B, "Liquefied Hydrogen Systems at Consumer Sites."

NFPA 55, "Compressed and Liquefied Gases in Portable Cylinders."

NFPA 70, "National Electric Code."

NFPA 496, "Purged and Pressured Enclosures for Electrical Equipment in Hazardous Locations."

Public Law 91-596, Section (5)(a)(1), OSHA General Duty Clause.

UCRL-AR-128970, "LLNL Pressure Safety Standard."

Uniform Mechanical Code, 1997.

Uniform Plumbing Code, 1997.

## 6.0 Resources for More Information

### 6.1 Contacts

For additional information regarding this document, contact the following:

- Area ES&H Teams
- Plant Engineering, Maintenance and Operations, Industrial Electronic Utilities

### 6.2 Lessons Learned

Refer to the Intranet address below for lessons learned applicable the topic discussed in this document:

[http://www-r.llnl.gov/es\\_and\\_h/lessons/lessons.shtml](http://www-r.llnl.gov/es_and_h/lessons/lessons.shtml)

### 6.3 Other Sources

29 CFR 1910.101, "Compressed Gases, General Requirements."

Compressed Gas Association, G-5.3, "Commodity Specification for Hydrogen."

Compressed Gas Association, G-5, "Hydrogen."

DOE Order 440.1A, "Worker Protection Management for DOE Federal and Contractor Employees." Attachment 2, "Contractor Requirement Document," Section 1-11, 13-16, 18 (delete item 18.a), 19 (delete item 19.d.3) and 22.

National Aeronautics and Space Administration, Chapter 6, "Hydrogen Propellant."

National Fire Protection Association, *Fire Protection Handbook* (latest edition).

National Safety Council, "Hydrogen Usage in the Laboratory," Data Sheet I-700, Rev. 86.

Peckner, D and I. M. Bernstein, "Stainless Steel in High Pressure Hydrogen Use," in *Handbook of Stainless Steels*, McGraw-Hill Book Co., NY (1977).

Matheson, *Gas Data Book*, 6th edition, Secaucus, NJ.